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Examination of Zinc Flue Dusts for Indium and Gallium

EXAMINATION OF ZINC FLUE DUSTS FOR INDIUM AND GALLIUM

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THE RARE BOOK & MANUSCRIPT UIUC

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INTRODUCTION

The present investigation has been undertaken with a view to discovering the presence of certain rare elements in flue dusts, and with particular reference to indium and gallium. The probability of their presence in flue dusts and especially in the zinc flue dust may be surmised from the facts that these elements have been found in the zinc blends and in other zinc bearing ores. Indium, for instance, was discovered by Reich and Richter in 1863 in the course of examination of the ores consisting mainly of the sulfides of arsenic, zinc and lead. In the United States the Bartlesville Zinc Company, Bartlesville, Oklahoma(1), has found alloys of indium and gallium appearing in "peculiar beads and drops, in appearance like mercury, which seem to sweat out of zinc-lead dross plates after these had been exposed to the weather for a time."

The methods employed in detecting these elements, while exclusively qualitative in nature, have all been aimed at the concentration of these elements in the form of chlorides. In view of the fact that these elements are found in very small amounts, it is evident that the ordinary qualitative precipitation and group classification will not prove conclusively either the presence or absence of the elements in the material under examination. This conclusion being borne out by other investigators engaged in the similar line of work, has led the author to resort to spectroscopic means which, with remarkable success and reliability, have already been pressed into service in connection

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with indium and gallium. The ordinary flame spectrum will not do. Recourse has been had to both spark and arc spectra.

The author has drawn freely upon text books as well as upon periodical literature and besides the references given by number in the body of the thesis, a bibliography will be found annexed.

Part I

General

History, Occurrence, and Properties of the Elements Sought.

Gallium

Historically, this metal, ~~was~~ discovered in 1875 by Lecoq de Boisbaudran by means of spectrum analysis, was predicted and named as eka-aluminium by Mendeleeff twenty years before its discovery. Boisbaudran(2) discovered gallium in the zinc blende of Pierrefitte in the Pyrenees and patriotically gave it the name which it now bears.

Gallium occurs in small amounts, chiefly in zinc blendes from Bensberg on the Rhine, Pierrefitte,(3) and in some American zinc blendes (1). The richest source is said to contain 0.016 grams per kilogram. Hartly and Ramage have shown the presence of gallium in some of the magnetites, in kaolin and bauxite, and in some manganese ores(4).

Gallium is solid at 23°, melts at 30.15°, frequently may be cooled to zero degree without again becoming solid. "It is grayish-white metal, crystallizing in octahaedra or in broad plates. It is quite brittle and gives bluish-gray marks on paper. It gives a very weak and fugitive flame spectrum, the spark spectrum shows two violet lines." "When heated in the air, or in oxygen it is but slightly oxidized, does not vaporize at white heat, soluble in acid and alkalies:and is attacked by halogens." Gallium is said to possess rare properties of occupying more volume in the solid than in the liquid condition.(5) The salts of gallium are colorless and for the most part soluble in water.

The alkalies and alkali carbonates precipitate the salts as hydroxide, perceptibly soluble in fixed alkali carbonates, more easily in ammonium hydroxide, and very readily in fixed alkalies. Tartrates hinder the precipitation of hydroxide. Hydrogen sulfide does not precipitate gallium salts from solutions, acid with mineral acids; from the acetate the white precipitate of gallium sulfide is precipitated.

Indium.

Indium was discovered spectroscopically in 1863 by Reich and Richter during the course of examination of zinc blende for Thallium.(6) "Instead of the thallium line, however, appeared one of indigo blue never before observed. The color suggested the name indium for the unknown element present."

Indium is found chiefly as sulfide, never native. The Freiberg zinc blende which is said to be the richest source for indium, contains one tenth of one percent. of indium. It is found in a few other places, (7) and (8), but in much smaller quantities. It has been detected in the flue-dust from ovens used for roasting zinc ores. In this country it has been found in the lead residue from zinc smelter.(1). And to add to it the results of the present investigation, indium has been found in zinc oxide, in bag-house dust, and in the flue-dust from copper and zinc smelting furnaces. According to Hartley and Ramage(3) it is present in siderites, in some manganese and tin ores, and in many pyrites.

Indium, like gallium, is a grayish white metal, very soft, and makes a good mark on paper. It is ductile, easily fusible, less volatile, less electro-positive than zinc or cadmium. Its most characteristic property is its spectrum, which affords the best means for its detection and identification. In the reaction of its compounds, indium deports itself similarly to gallium, iron and aluminium. Indium salts are precipitated by alkalies as indium hydroxide, insoluble in excess. The earlier record shows that indium hydroxide is soluble in excess of the fixed alkalies but the recent investigations(5) point to the contrary. The author has found it quite insoluble in excess of the fixed alkalies. Hydrogen sulfide does not precipitate indium from salts acid with mineral acids. It is, however, precipitated from a solution acid with acetic acid. Potassium ferricyanide and potassium sulfocyanate do not precipitate indium.

Source of Materials

The materials used consisted of flue-dusts, zinc oxide and ore. Blende roaster flue-dust and zinc oxide were from the Mineral Point Zinc Company, Depue, Illinois. Prolong blue powder and ore came from the Hegeler Zinc Company, Danville, Illinois. Bag-house dust and blast-furnace flue-dust were obtained from the American Smelting and Refining Company, East Helena, Montana. Zinc roaster flue dust was sent by the Anaconda Copper Manufacturing Company, Great Falls, Montana. In order to explain where the actual samples were obtained, the following brief account of the smelting process may serve the

purpose. In the usual process, the ore is fed into the blende roaster where it is oxidized to zinc oxide. The sample of zinc oxide above referred to was taken at this stage of the process. The sulphur dioxide which goes up the flues is usually utilized in manufacturing sulphuric acid. In order that the sulphur dioxide may be available for this purpose, the dust must be removed and this is accomplished by means of large dust-collectors, or by a bag-house. The dust that accumulates in the dust collectors is called blende roaster flue-dust; if the ore used is other than zinc sulphide, the dust is collected in a bag-house and is called bag-house dust. The zinc oxide as it comes from the roaster is mixed with anthracite coal and charged into clay retorts, where zinc oxide is reduced to metallic zinc which is distilled off and is collected in clay condensers placed at the end of the retort. A prolong extends from the end of the condenser, and a certain amount of prolong blue powder collects here. This consists of coal and zinc dust, together with some zinc oxide.

General Method of Analysis.

The general method of analysis consisted in bringing the material into solution either by acid treatment or by fusion, and in separating the elements into their qualitative groups according to the following plan: After the separation of first group the elements of the second and third groups were precipitated by use of metallic zinc, filtered, dissolved in a small amount of hydrochloric acid and in proper acidity were precipitated

by hydrogen sulphide. The precipitate was filtered. While the residue contained the second group, the third group remained in the filtrate. The filtrate containing the third group was evaporated to a small volume, and examined for indium and gallium by flame, spark and arc spectra respectively. In cases where Indium or gallium was shown to be present, the filtrate was treated with excess of ammonium hydroxide which precipitated indium, iron, zinc and other metals as hydroxides; zinc being largely soluble in excess of the precipitant passes into solution so that if the precipitate is now filtered zinc remains in the solution. Indium was next separated from the rest of the metals by the cyanide method; (see page 18).

Apparatus

The forms of apparatus used in the course of examination of the materials were the ones usually employed in qualitative and quantitative work. In addition to the ordinary apparatus, the spectroscope was largely used. The apparatus used for producing spark and arc spectra was in principle identical with that employed by Dennis and Bridgman(9), except some differences in technique that had to be developed to meet the experimental requirements. The modification consisted in the construction of the electrodes and in the length of the spark. In the case of arc spectrum, however, the difference lay in employing the solid substance against the use of solution evaporated in the cup of the lower electrode as the authors above referred to had used. The spark spectrum apparatus consisted of a Krüss spectroscope, induction coil capable of giving a spark over one inch in length,

and glass cups for holding the solutions. The electrodes were made of platinum wire, 1.5 mm. in diameter, fused through the ends of glass tubing 8 mm. in diameter. The upper electrode consisted of glass tubing with platinum wire fused thoough the lower end of it, and projecting about 6 mm. from that end. The lower electrode was made by fusing platinum wire into glass tubing, and then cutting off the tube about 8 mm. from the fused end. The cup so formed is capable of holding 5-6 drops of a solution. With the proper adjustment of the length of the spark, the electrodes thus prepared yielded the most satisfactory results. After several trials it was found that a spark 5-6 mm. in length was the best for producing the most steady and reliable spectrum; the longer spark becomes distorted and this disturbs the stability of the position of the spectrum lines. If the spark is longer than 6 mm. it happens that the spark suffers a distortion, with the result that the spark continually appears and disappears, so that the spectrum lines are never visible for more than a fraction of a second. Moreover, the longer spark abruptly shifts its position along the rim of the cup of the lower electrode. This also renders the observation unreliable. For the observation of arc spectrum a Hilger wave-length spectrometer was used. The arc was formed between graphite electrodes 15 mm. in diameter. The lower end of the upper electrode was roughly pointed. A depression was hallowed out in the upper end of the lower electrode. Before using these electrodes, they were boiled in hydrochloric acid and then washed with boiling water. A small portion of the material to be examined was placed in the depression and examined.

up with 50 cc. of hydrochloric acid to which a little nitric acid was added to oxidize the metals.

The solution thus obtained was diluted to 500 cc., neutralized with ammonium hydroxide, and brought to proper acidity by adding to it 15 cc. of concentrated hydrochloric acid. It was warmed and treated with a rapid stream of hydrogen sulfide to precipitate the metals of the second group. The solution was now diluted to 1000 cc. with cold water and again treated with hydrogen sulfide. After the precipitation was complete, the precipitate was filtered off, washed with water containing hydrogen sulfide, and discarded. The filtrate was boiled to free it from hydrogen sulfide dissolved in it, cooled to room temperature, and treated with decidedly large excess of ammonium hydroxide, which precipitated the metals of the third group as hydroxides, the excess of ammonium hydroxide acting as a solvent dissolved most of the zinc hydroxide so that almost all of the zinc can thus be gotten rid of. The precipitate was filtered and dissolved in hydrochloric acid.

Spark Spectrum.

Detailed manipulation of the apparatus employed in the examination of a substance for its spectrum has already been referred to.(9) By means of a glass tube drawn from one end, a few drops of a known solution of indium and gallium chlorides were introduced into the cup of the lower electrode which has been fully described under Apparatus (which see). The current was then turned on, and spectrum was observed. After several trials, it was found that the best spectrum as to its steadiness and intensity could only be obtained when the length of the spark was very

Part II

Qualitative Analysis

Sample number one.

The first sample analyzed was zinc oxide from Mineral Point Company, Depue, Illinois. A mixture of three parts of concentrated nitric acid and one part of water was found to dissolve the sample completely and rapidly. 500 cc. nitric acid of the above strength was brought to boiling and a sample of 50 grams of the oxide was added, the boiling was continued until all of the sample had dissolved. The solution was next treated with excess of sulphuric acid, and after evaporating to dryness, was taken up with 500 cc. water. On warming, most of the solid passed into solution. The residue was filtered and washed with small amounts of water. In this way, lead was completely removed. 200 cc. concentrated hydrochloric acid were then added to the filtrate, the whole transferred to a 1500 cc. beaker, and was placed on the steam bath. A plate of pure zinc four by six inches and about one-fourth of an inch in thickness was gently introduced into the solution to precipitate indium, gallium, iron, etc. The zinc plate was left in contact with the solution on the warm steam bath for a period of two days. After two days, the displacement of the metals from the solution by the zinc was found to be complete. The zinc plate was then taken out of the solution, the precipitate on the plate was rubbed loose, and washed into the solution. A small amount of dilute sulphuric acid was added to the solution to dissolve basic zinc chloride that had formed. The metallic precipitate was then filtered, washed with water, and was taken

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short. This, of course, has already been pointed out by Sir W. Crookes(11). A spark about 6 mm. long, as already recorded, was the best. During the observations, as the solution evaporates, the length of the spark, of course, materially changes, but does not reach to a point where it would suffer distortion. After this had successfully been attained, the spectrum of indium and gallium from known solution was mapped out with reference to D line.

After the electrodes had been washed with hydrochloric acid and with distilled water to free them from any adhering material, 7-8 drops of the solution (unknown) were similarly introduced into the cup of the lower electrode. On observation, there appeared one of the indium lines, faint to begin with, but growing intense as the solution evaporated. Repeated investigations confirmed the first observation.

Arc Spectrum.

So far as the spark spectrum was concerned, the author was sure that it was nothing but an indium line, but by means of the arc spectrum its wave length had to be measured to ascertain as t to which one of several lines of indium it was, although, in all probability it was 4511.0. The solution was next evaporated to dryness, and a small amount of the solid was placed in the depression which was hollowed out in the upper end of the lower electrode that was, in turn, a graphite rod.(9). On examination of the spectrum, it proved to be indium line of wave length 4511.0 rather intense, but did not last very long. It, however, conclusively proved the presence of indium in the sample.

Sample Number Two.

The sample number two was zinc roaster flue-dust from the Anaconda Manufacturing Company, Great Falls, Montana. The only difference in the procedure and analysis between the sample number two and sample number one was in bringing the material into solution. In this case, as in the following, no acid of any strength seemed to dissolve the sample completely. A fusion mixture consisting of 3 grams of sodium peroxide, and one gram of sodium carbonate for each gram of the sample proved very efficient(9). A 25-gram sample was fused in a nickle crucible with the above substances, dissolved in water, neutralized with nitric acid, and was treated with ammonium hydroxide to precipitate indium, gallium, iron, etc., so that if a large excess of ammonium hydroxide is used and the precipitate filtered, most of the zinc and all of the soluble alkali pass into the filtrate. From this point on the procedure was exactly the same as in sample number one.

The spectrum analysis showed that this sample also contained indium. In addition to this, one of the gallium lines was also noticed. On further observation it proved to be the gallium line of wave length 4172.0. Since this sample has been found to contain a very large amount of iron that makes up the bulk of the precipitate, the line observed was comparatively faint.

Samples Number Three and Four.

The samples number three and four were from the same company (American Smelting and Refining Co., East Helena, Montana), but

secured from different parts of the smelter. Number three was bag-house dust and number four ~~from~~ blast furnace flue-dust. The analyses of these were exactly identical in all respects with those of sample number two. A 25-gram sample of each of these was used. Here again spectrum analysis showed the presence of indium in the bag-house dust. In the case of blast-furnace flue dust, extremely faint line of indium was observed,which could not be taken to indicate more than mere traces of indium in the sample.

Samples Number Five and Six.

They were prolong blue powder and ore which came from the Hegeler Zinc Company, Danville, Illinois. Prolong blue powder required no fusion treatment. A 20-gram sample was analyzed in exactly the same manner as sample number one. A 71-gram finely ground sample of the ore, however, required the fusion treatment according to sample number two. The spectroscope analysis of both of these samples showed no evidence of the presence of either indium or of gallium.

Sample Number Seven.

The sample number seven was blende roaster flue-dust from the Mineral Point Zinc Company, Depue, Illinois. A 10-gram sample was analyzed according to the plan used for analysis of sample number two(which see). In this case, too, no evidence of the presence of either indium or of gallium was found.

Discussion of the Available Methods for the Separation of Iron from Indium.

A number of methods that are found in the literature for the separation of iron from indium were tried without success. This is, in part, due to the fact that a large number of our analytical methods alleged to produce quantitative results do very well when the element sought is present in a large amount, but fails utterly when the element sought is present in an exceedingly small amount. This is especially true of the methods for the separation of iron from indium. Scarcity of indium is due not so much to its limited distribution as it is to the lack of a sharp method for its extraction from the ores or flue dusts. The best conclusion, however, can only be drawn when a brief but clear discussion of the various methods has been presented.

The separation of indium from metals other than iron presents little or no difficulty. This, however, is not the case when iron is present in large quantities. And it is with this problem that the author is concerned. Analytically there are four or five possibilities for the separation of iron from indium:

1. To find a reagent that precipitates indium, leaving iron in the solution.

2. To use a reagent which would precipitate iron but not indium.

3. To find a precipitant which precipitates both, but redissolves one of them, preferrably iron, when added in excess.

4. Electrolytic deposition.

5. Extraction of ferric sulfocyanate with ether.

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[illegible]

[illegible]

1. [illegible]

2. [illegible]

3. [illegible]

a. [illegible]

b. [illegible]

Of all the methods that have, with some degree of success, been used to separate iron from indium, five come under the first possibility:

1. "Winkler obtained a separation by the fractional precipitation of the sulfide, the indium sulfide being less soluble than the iron sulfide." (12)

2. Bayer treated a solution of the mixed chlorides of indium and iron with sodium sulfite, which precipitated indium as indium basic sulfite. In order to purify the precipitate, it was dissolved in sulfurous acid and basic indium sulfite was again precipitated on boiling. (13)

3. Weselsky passed sulfur dioxide into a solution of the chlorides of indium and iron, and then by adding barium carbonate to the solution, obtained a precipitate of indium hydroxide together with traces of iron and zinc. (14)

4. "Meyer treated the material that contained indium and iron with sodium carbonate until neutral and then with a solution of potassium cyanide until the precipitate first formed was redissolved. The solution thus formed was diluted with ten volumes of water and boiled. This decomposed the potassium indium cyanide and indium hydroxide was precipitated, while the iron remained in the solution as potassium ferri- or ferrocyanide."

5. Renz took up the material containing indium and iron chlorides with absolute alcohol and treated the alcoholic solution with pyridine, which precipitated indium as ($InCl_3 . 3C_5H_5N$) but left iron in solution. (17)

A sound criticism as to the nature and relative success of all these methods, except pyridine which the author tried without success, is given by Mathers in his paper on "Separation of Iron From Indium."(19) His conclusions as to the unreliability and inadequacy of all these methods agree entirely with the unsuccessful efforts the author has made in trying to separate iron from indium. The author has tried the methods, 2, 3, and 5, with negative results. It is to be emphasized that these methods, whatever may be their intrinsic worth, fail of their service when the ratio of indium to iron is extremely small. Theoretical considerations borne out by the experimental results point to the same conclusion. The indium compounds resulting from precipitation or crystallization (by their very nature as may be expected from the periodical table) are not absolutely insoluble in the solvents commonly employed. Now if the amount of indium in the sample is exceedingly small and the volume of the solution containing both indium and iron is considerably large, the precipitate to be obtained by the use of a reagent would hardly be more than that needed to satisfy the requirements of solubility. An attempt to concentrate the solution to make the amount of indium compound present in the solution exceed the solubility product results not in the precipitation of indium, but that of iron, so that indium remains distributed: some in the solution, some with the precipitate. These methods, like all other gravimetric methods, are not free from defects inherent in them. It must be remembered that there are very few ideal gravimetric methods that

have been successfully used in quantitative analysis.

The literature on indium shows that there is no Successful method that could be grouped under the second possibility. The author has, however, made an unsuccessful attempt to discover one. Potassium ferricyanide does not precipitate indium from the solution of its salts, but it does precipitate iron when it is in the solution in the ferrous condition. A 50 c.c. solution of ferrous chloride containing a few drops of indium chloride was treated with potassium ferricyanide, the resulting precipitate filtered and washed. Both the precipitate and filtrate were spectroscopically examined. Spectroscopic observations showed that indium was present more in the precipitate than it was in the filtrate. This is apparently due to adsorption. Any method that may be devised on this plan will apparently possess this serious drawback.

There exists no method that may be included in the third possibility. An attempt has, however, been made to devise one. Ferrous hydroxide dissolves in excess of potassium cyanide with the formation of potassium ferrocyanide, but nothing is known as to the solubility of indium hydroxide in potassium cyanide. Freshly precipitated indium hydroxide was treated with excess of potassium cyanide; indium hydroxide was found to be insoluble in excess of potassium cyanide. Next, 2 c.c. of very weak solution of indium chloride was mixed with 30 c.c. of ferrous chloride prepared by reducing ferric chloride by metallic zinc, so that there was a considerable quantity of zinc in the solution. The solution was then treated with a large excess of ammonium hydroxide, followed

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by the addition of a saturated solution of potassium cyanide. All but a very small amount of precipitate went into solution. The precipitate was filtered, washed and taken up with 5 c.c. of hydrochloric acid. Spectroscopic examination showed that both the precipitate and filtrate contained indium, zinc and iron.

So far as electrolytic deposition is concerned, the author has made no attempt. According to Mathers(19) iron always deposits with indium. Extraction of ferric sulfocyanate with ether has, of course, been tried. In the presence of a large amount of iron this method also fails.

The method by which the author has been able to separate indium from iron is based upon the fact that if a solution of chlorides of indium and iron be treated with an excess of sodium cyanide, iron passes into a complex anion while indium evidently remains as cation, since it is precipitable by alkalies. It might appear that this method is identical with Meyer's(13) potassium cyanide method already referred to. This, however, is not the case. While Meyer treats ferric chloride solution with excess of potassium cyanide, the author first reduces the ferric chloride to ferrous chloride and then adds cyanide. In fact, these methods have nothing in common, except the use of the cyanide. Mathers, who has tried Meyer's method, concludes that it is inadequate.

The method here proposed is as follows:

A 50 gram sample of zinc roaster flue-dust was treated according to the scheme described in connection with sample number

two. The resulting solution of the chlorides of indium and iron was treated with excess of sodium hydroxide to remove most of the zinc that was present in the sample. The precipitate consisting of indium hydroxide and ferric hydroxide was filtered, washed, and then taken up with hot dilute hydrochloric acid. The resulting solution was boiled, and treated with a rapid stream of hydrogen sulfide in order to reduce the iron to the ferrous condition. The solution was quickly filtered and introduced through a separatory funnel into a liter flask containing 200 c.c. of a saturated solution of sodium cyanide. The flask was provided with a two-hole rubber stopper fitted with a 500 c.c. separatory funnel and an exit tube. The contents of the flask were next treated with dilute hydrochloric acid until just neutral. After this had been accomplished, a large excess of ammonium hydroxide was added, and a solution was boiled for five minutes. The boiling helped the precipitate of indium hydroxide settle. After it had cooled to the room temperature, the precipitate was filtered, washed with water, and taken up with hydrochloric acid. The resulting solution was tested for ferric chloride with potassium sulfocyanate. It gave only a very weak test for iron. This, however, necessitated a second treatment. The operation was repeated, and this time the precipitate was colorless and when dissolved in hydrochloric acid, gave faint or negative test for iron.

A word of precaution may be added. The success of the method, in a large measure, is dependent upon the complete reduction of the ferric to ferrous iron and upon careful neutralization of

the solution; excess of the acid decomposes a little sodium ferrocyanide which, besides rendering the filtration much more difficult, involves some loss of indium.

Quantitative Analysis.

For the quantitative determination of the content of indium in the material, precisely the same procedure as that given on page 18 has been carried out. The indium hydroxide obtained in this way was filtered on ashless filter paper, dried and ignited in a tared porcelain crucible until the filter paper was burned. The crucible was cooled and its contents just moistened with nitric acid and was ignited again to constant weight. Four samples of zinc roaster flue-dust from the Anaconda Copper Manufacturing Company, Great Falls, Montana, have been analyzed and results of the four determinations are as follows:

No. of sample	Wt. of sample Grams	In_2O_3 Grams	% of In_2O_3
1	50	.0404	.0808
2	50	.0442	.0888
3	50	.0404	.0808
4	50	.0338	.0676
Average			.0795

Summary

1. Of the seven samples of flue dusts, residues and ore examined for indium and gallium, four have been found to contain indium. Of these four, one contains both indium and gallium.

2. A brief discussion of the various methods for the separation of indium from iron has been included.

3. An entirely new method for the separation of indium from iron has successfully been developed.

4. Quantitative determinations have shown that the content of indium oxide in the material examined is on the average .08 percent.

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